

# High Level Computational Chemistry Approaches to the Prediction of the Energetic Properties of Chemical Hydrogen Storage Systems

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**Chemical H<sub>2</sub> Storage Center of Excellence**

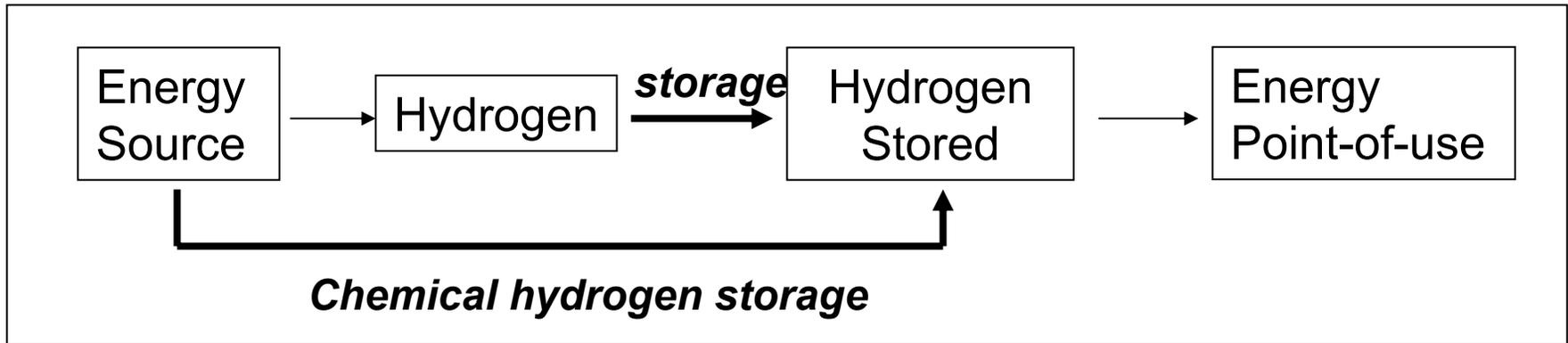
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Robert Ramsay Chair Fund



Shelby Hall

# The Promise of Chemical Hydrogen Storage



- Chemical reaction releases H<sub>2</sub> at suitable pressures and temperatures
  - Reaction *thermodynamics* dictate max. H<sub>2</sub> pressure as function of T – need to manage both  $\Delta H$  and  $\Delta G$
  - Reaction *kinetics* dictate rate of release of H<sub>2</sub> – need to develop catalysts to control kinetics and release
  - Enables significant storage capacity at “zero” pressure – improve safety issues
- Infrastructure based on a solid or liquid fuel
  - Spent fuel regenerated “off-board” using industrial chemical engineering process technology to reduce cost
  - Bypass direct consumer contact with gaseous hydrogen
  - Hydrogen need only appear when required at the fuel cell anode

# What's needed for chemical accuracy?

## Example: reaction energetics, catalyst design, or separations systems for hydrogen storage

Catalyst *design* will require quantitative information about *transition states* for critical reaction processes in catalysis. These are *only* accessible by computational methods, which hold the key to the fundamental understanding of catalytic processes thus enabling reliable catalyst design

Predict equilibrium chemistry: *Selectivity*

Change in  $K_{eq}$  @ 298 K

$K_{eq} = 1$	50:50	$\Delta G = 0$ kcal/mol
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$K_{eq} = 10$	90:10	$\Delta G = 1.4$ kcal/mol
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$K_{eq} = 100$	99:1	$\Delta G = 2.8$ kcal/mol
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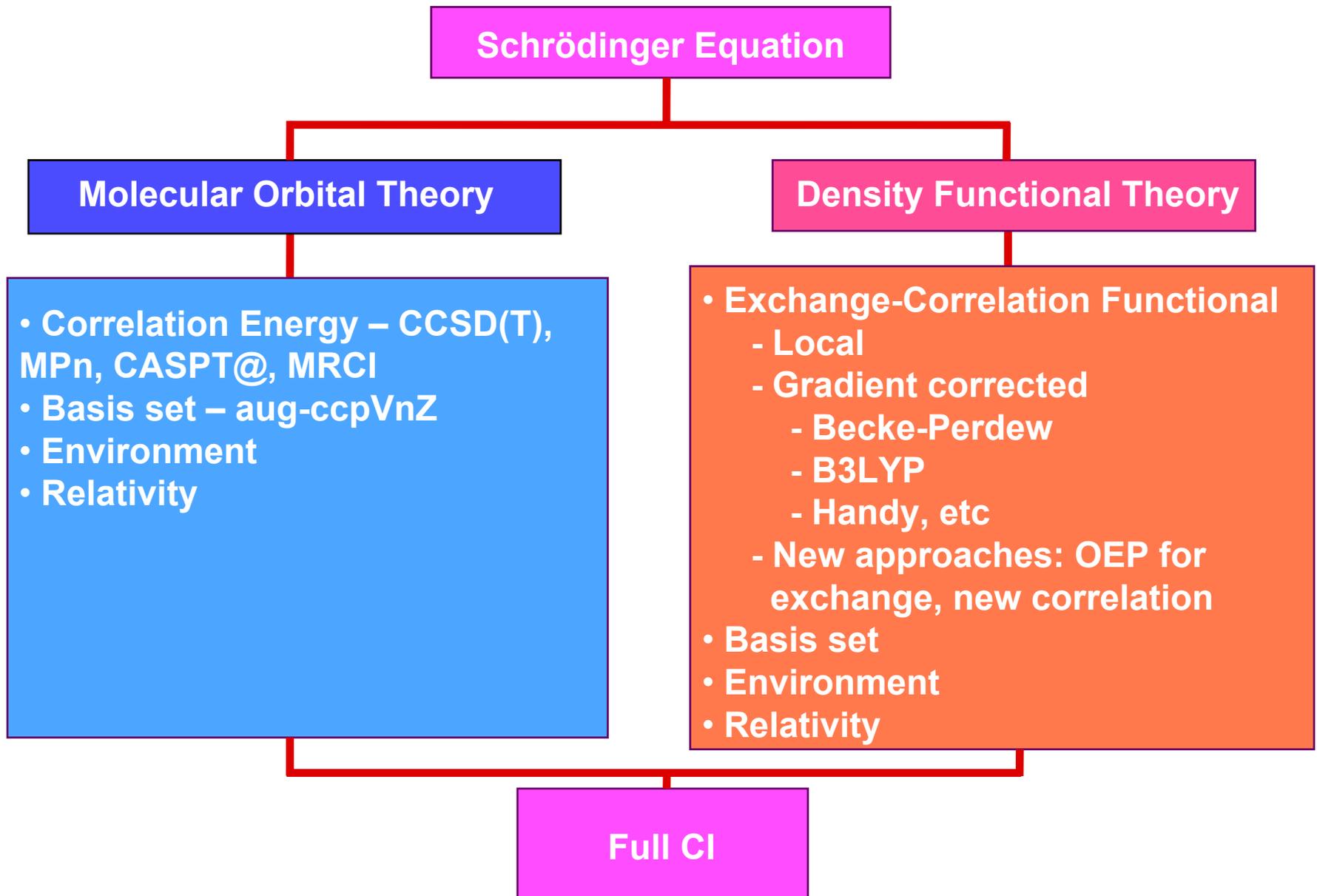
Predict accurate rates: *Reactivity*

Absolute Rates @ 298 K

Factor of 10 in rate @ 25°C is a change in  $E_a$  of 1.4 kcal/mol

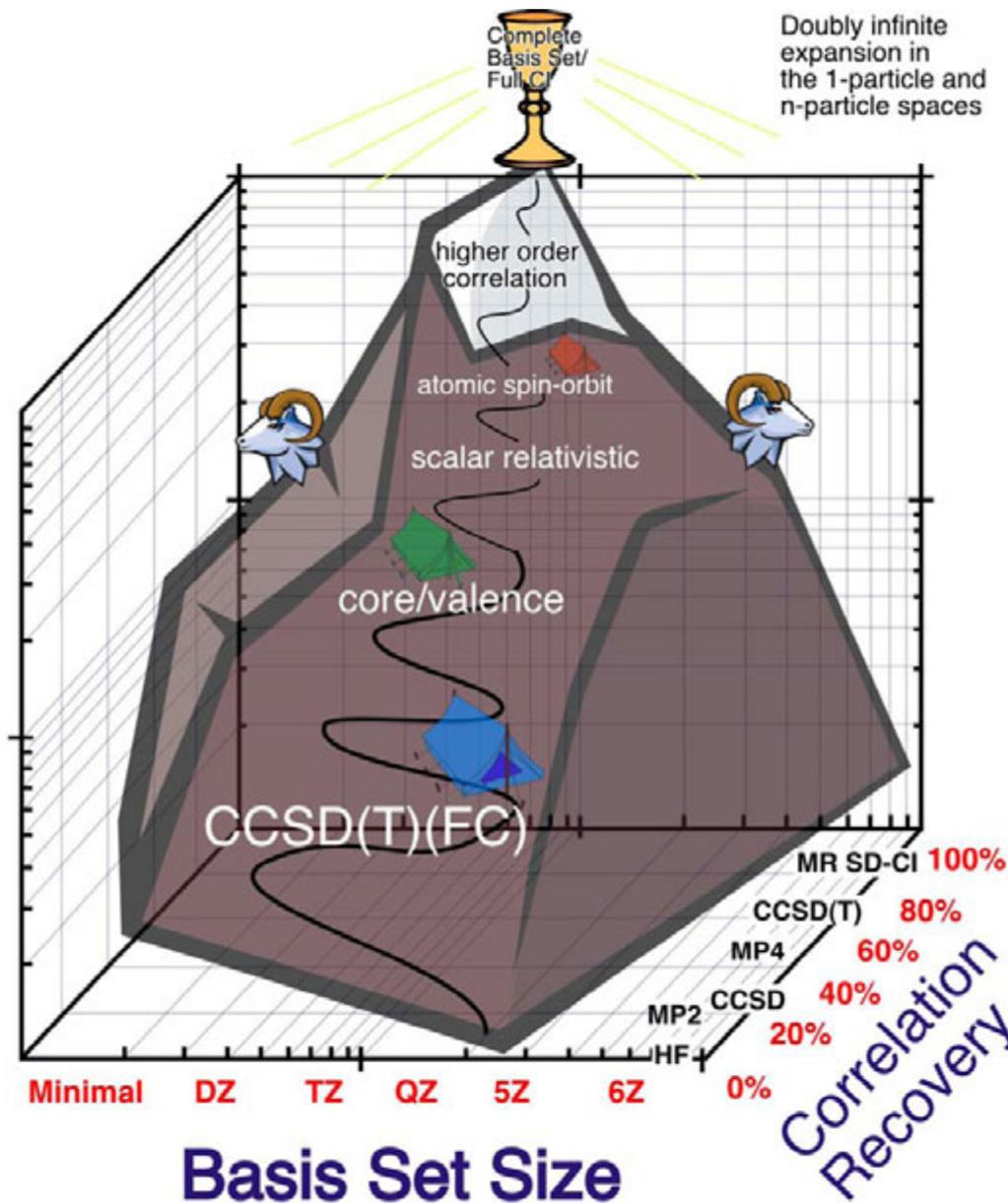
Molecular design will require being able to do accurate calculations and/or being very clever!

# Solving the Schrödinger Equation



# High level electronic structure theory

Computational Cost



Total atomization energy at the CCSD(T) level extrapolated to the complete basis set limit using the augmented-correlation consistent basis sets

- + core-valence corrections
- + scalar relativistic
- + spin orbit
- + zero point energy
- + thermal corrections (0 → 298K)

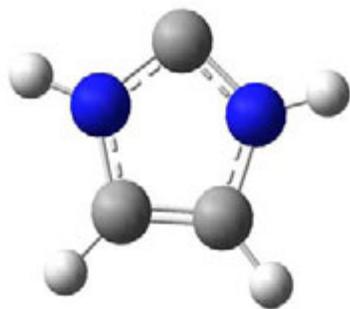
Use atomic heats of formation to get molecular heats of formation

Use CCSD(T) or MP2 geometries

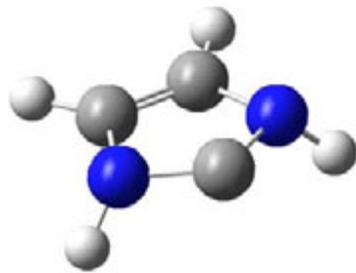
IP's and EA's

# Carbenes for H<sub>2</sub> Storage Systems

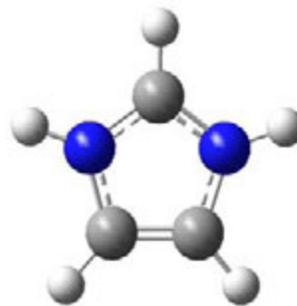
Do carbon-based systems exist that have more accessible CH bonds than traditional hydrocarbons?  $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$   $\Delta\text{H}(298) = 32.6 \text{ kcal/mol}$



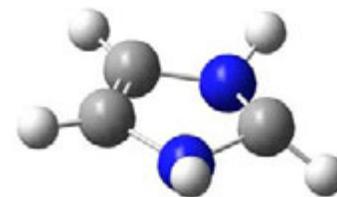
carbene



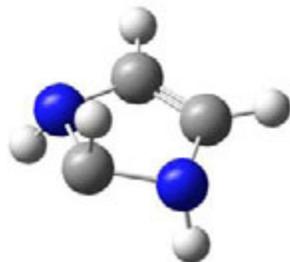
<sup>3</sup>carbene



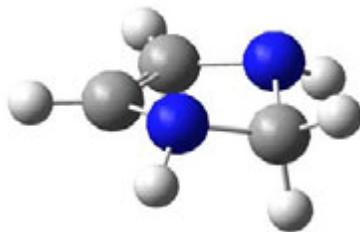
carbeneH<sup>+</sup>



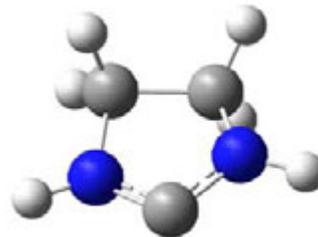
carbeneH



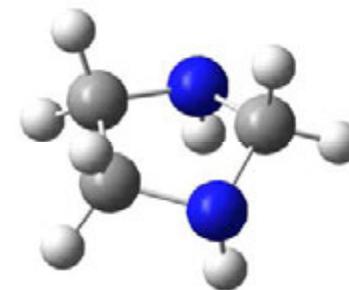
carbeneH<sup>-</sup>



carbeneH<sub>2</sub>



carbeneH<sub>6</sub>



carbeneH<sub>8</sub>

Based on Arduengo's stable carbene

# Calculated atomization energies for carbenes

<b>Molecule</b>	<b>CCSD(T)/CBS</b>	$\Delta E_{\text{ZPE}}$	$\Delta E_{\text{CV}}$	$\Delta E_{\text{SR}}$	$\Delta E_{\text{SO}}$	$\Sigma D_0$ (0K)
carbene	922.38	43.78	3.93	-1.15	-0.24	881.14
<sup>3</sup> carbene	834.15	45.10	3.78	-1.23	-0.24	791.36
carbH <sub>2</sub>	1052.90	57.85	3.99	-1.15	-0.24	997.65
carbH <sup>+</sup>	865.93	52.11	4.27	-1.21	-0.24	816.64
carbH <sup>-</sup>	952.83	47.58	3.55	-1.18	-0.24	1125.84
carbH	962.78	53.23	4.11	-1.24	-0.24	912.18
CarbH <sub>6</sub>	1047.49	57.93	3.85	-1.20	-0.24	907.38
carbH <sub>8</sub>	1196.52	73.07	3.87	-1.24	-0.24	1,125.84

# Carbene CCSD(T) Heats of Formation (kcal/mol)

<b>Molecule</b>	<b>CCSD(T) (0K)</b>	<b>CCSD(T) (298K)</b>
carbene	60.4	55.4
<sup>3</sup> carbene	150.2	145.9
carbeneH <sub>2</sub>	47.1	41.5
carbeneH <sup>+</sup>	176.5	171.6
carbeneH <sup>-</sup>	85.8	80.7
carbeneH	81.0	75.7
CarbeneH <sub>6</sub>	52.8	46.8
CarbeneH <sub>8</sub>	22.2	14.3

“Heats of Formation of the Arduengo Carbene and Various Adducts Including H<sub>2</sub> from Ab Initio Molecular Orbital Theory,” D. A. Dixon and A. J. Arduengo, III, *J. Phys. Chem., A* **2006**, *110*, 1968

# Carbene Reaction Energetics for H<sub>2</sub> storage at 298K in kcal/mol to $\pm 1$ kcal/mol



Adding H<sub>2</sub> to the carbene is exothermic by 14.9 kcal/mol -- very nice in managing release because we can use  $\Delta G$  to pull it off using Le Chatelier's Principle.  $T\Delta S(298\text{K}) = +8.2$  kcal/mol



The PA of the simplest carbene is 249.1 kcal/mol. Very basic!



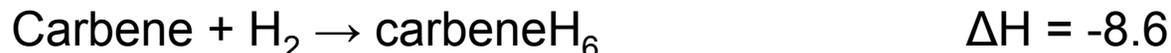
The singlet triplet splitting of the carbene is very large!



The C-H bond energy for adding an H to the carbene shows a weak C-H bond.



Addition of H<sup>-</sup> to the simplest carbene leads to autodetachment of the e<sup>-</sup>.



Adding H<sub>2</sub> to hydrogenate the double bond is exothermic by only 9 kcal/mol as compared to -31 kcal/mol for hydrogenation of C<sub>2</sub>H<sub>4</sub>.



Adding H<sub>2</sub> to the hydrogenated carbene is quite exothermic – develop carbene reactivity scale.

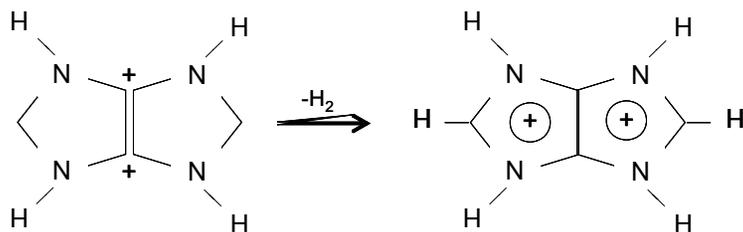
## Hydrogenation energies (kcal/mol) of carbenes

<b>Reaction</b>	<b><math>-\Delta H_{\text{rxn}}</math> (298K)</b>
carbene + H <sub>2</sub> → carbeneH <sub>2</sub>	14.9
carbeneH <sub>6</sub> + H <sub>2</sub> → carbeneH <sub>8</sub>	32.6
<sup>1</sup> CF <sub>2</sub> + H <sub>2</sub> → CF <sub>2</sub> H <sub>2</sub>	62.2
<sup>3</sup> carbene + H <sub>2</sub> → carbeneH <sub>2</sub>	101.3
<sup>3</sup> CF <sub>2</sub> + H <sub>2</sub> → CF <sub>2</sub> H <sub>2</sub>	108.2
<sup>3</sup> CH <sub>2</sub> + H <sub>2</sub> → CH <sub>4</sub>	110.9

# Heteroatom Organic Systems for Hydrogen Storage: The “Alabama Approach”

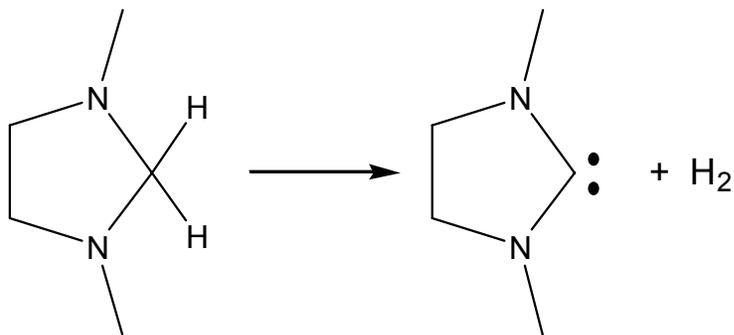
## Other ways to release hydrogen from dihydroimidazoles, not previously known

1,5 elimination to give fused diimidazolium rings:



- Hydrogen elimination is symmetric (non-polar (\*))
- No metal catalyst required (substituents on N, C)
- Endothermic dehydrogenation,  $P_{\text{eq}} < 1 \text{ atm}$

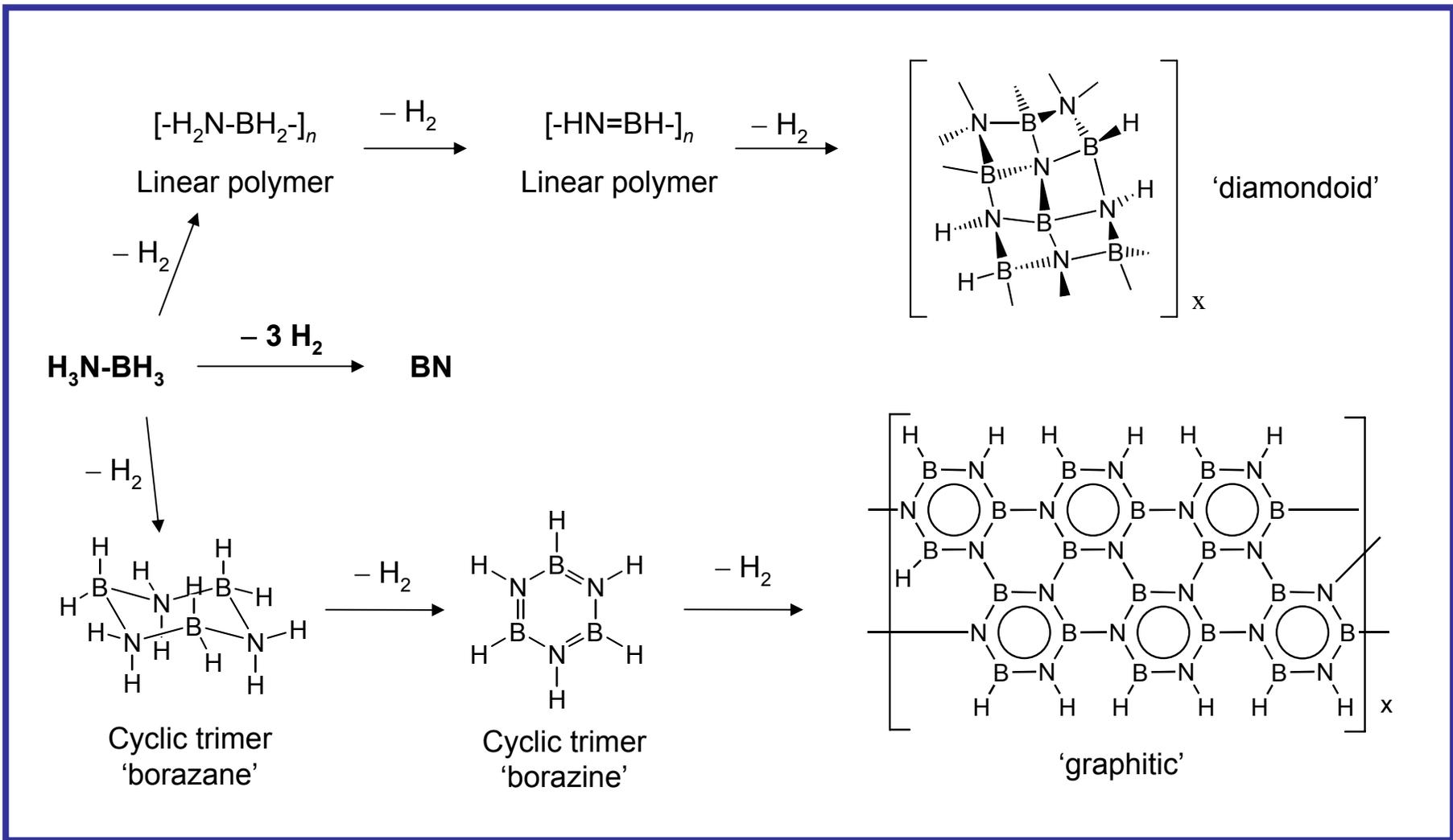
1,1 elimination to give carbene products:



- Hydrogen elimination is symmetric (non-polar (\*))
- Metal catalyst required (substituents on N, C)
- Endothermic dehydrogenation,  $P_{\text{eq}} < 1 \text{ atm}$

Bo Arduengo

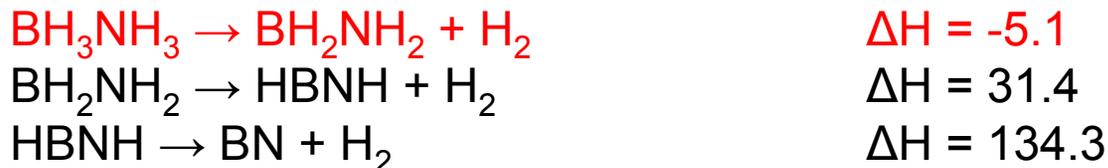
# Hydrogen Production Using Ammonia-Borane



Collaborators: Fran Stephens & Tom Baker (LANL)

# Reaction Energies in borane amines in kcal/mol @ 298K for chemical hydride storage

- Reaction energies for the sequential release of H<sub>2</sub> from borane amines (gas phase) based on the most accurate heats of formation now available – our calculated values.



- BH<sub>3</sub>NH<sub>3</sub> will be a good source of H<sub>2</sub> as the release of H<sub>2</sub> from this species is not far from thermoneutral due to the donor-acceptor bond. Cannot make T too high as entropy also favors release of H<sub>2</sub>.
- The reaction energies for forming BN/C<sub>2</sub> and BHNH/CHCH are ~ equal. Similarity of the isoelectronic C<sub>2</sub>H<sub>2m</sub> and BNH<sub>2m</sub> systems except for m = 3. Due to differences in σ bond energies.
- Can the salt [BH<sub>4</sub><sup>-</sup>][NH<sub>4</sub><sup>+</sup>] serve as an H<sub>2</sub> storage system? Estimate the lattice energy, U<sub>L</sub>, of the salt from the empirical expression dependent on the volume.  
$$\begin{array}{l} [\text{BH}_4^-][\text{NH}_4^+] (\text{s}) \rightarrow \text{BH}_3\text{NH}_3(\text{g}) + \text{H}_2 \quad \Delta\text{H}(0\text{K}) = 0.2 \text{ kcal/mol} \\ [\text{BH}_4^-][\text{NH}_4^+] (\text{s}) \rightarrow \text{BH}_3\text{NH}_3(\text{s}) + \text{H}_2 \quad \Delta\text{H}(0\text{K}) = -16.8 \text{ kcal/mol} \end{array}$$

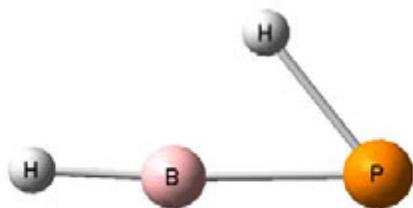
- We need to predict condensed phase interactions. Strong dipolar interactions.

“Thermodynamic Properties of Molecular Borane Amines and the [BH<sub>4</sub><sup>-</sup>][NH<sub>4</sub><sup>+</sup>] Salt for Chemical Hydrogen Storage Systems from Ab Initio Electronic Structure Theory,” D. A. Dixon and M. Gutowski, *J. Phys. Chem. A*, **2005**, *109*, 5129

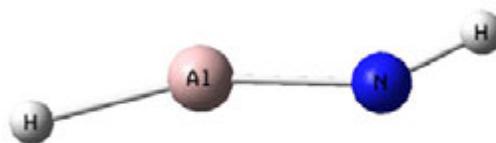
# Bond Energies in kcal/mol for chemical hydride storage

Reaction	B.E. ( $\Delta H(0K)$ )	Bond
$BH_3-NH_3 \rightarrow BH_3 + NH_3$	25.9	dative
$CH_3-CH_3 \rightarrow 2 CH_3$	87.9	C-C $\sigma$
$BH_2=NH_2 \rightarrow BH_2 + NH_2$	139.6	B-N $\pi$ + B-N $\sigma$
$CH_2=CH_2 \rightarrow 2 CH_2 (^3B_1)$	171.9	C-C $\pi$ + C-C $\sigma$
$BH_2-NH_2 \rightarrow BH + NH$	178.5	
$HCCH \rightarrow 2 CH$	228.1	

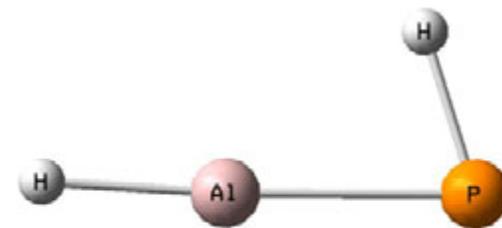
- For  $C_2H_4$ , the C-C  $\pi$  bond is  $\sim 65$  kcal/mol giving a C-C  $\sigma$  bond energy of 107 kcal/mol. Due to  $sp^2-sp^2$  bonding, not  $sp^3-sp^3$  bonding.
- Estimate the B=N  $\pi$  bond energy by calculating the rotation barrier in  $BH_2NH_2$ 
  - Electronic contribution = 31.99 kcal/mol
  - Zero point contribution = 2.02 kcal/mol
  - Barrier at 0K = 30.0 kcal/mol
- Gives a very strong B-N single bond of 109.6 kcal/mol, comparable to the C-C  $\sigma$  bond. The high B-N  $\sigma + \pi$  bond energy in  $BH_2NH_2$  is consistent with the fact that it does not release  $H_2$  readily.



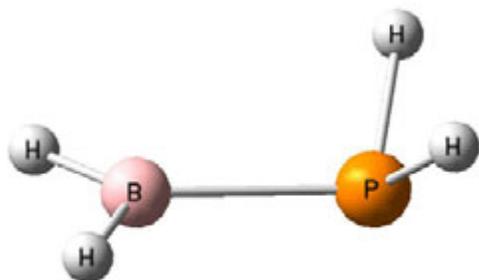
HBPH



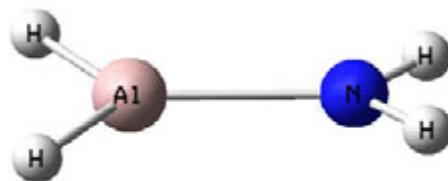
HAINH



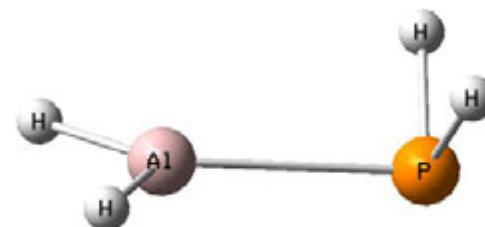
HAIPH



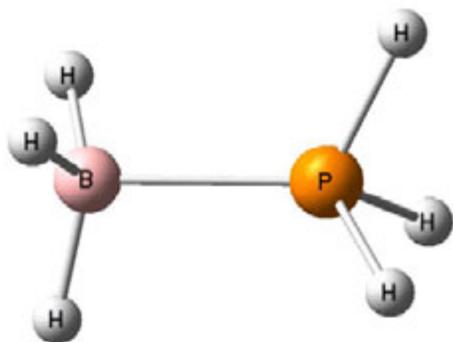
H<sub>2</sub>BPH<sub>2</sub>



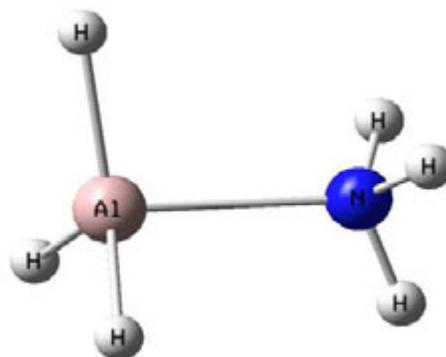
H<sub>2</sub>AINH<sub>2</sub>



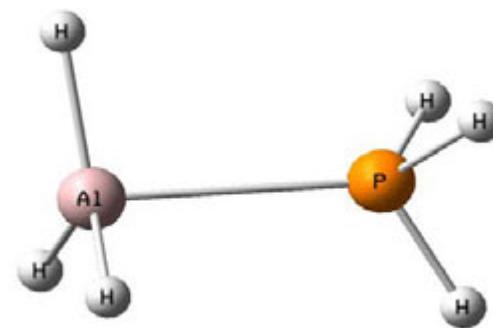
H<sub>2</sub>AIPH<sub>2</sub>



H<sub>3</sub>BPH<sub>3</sub>



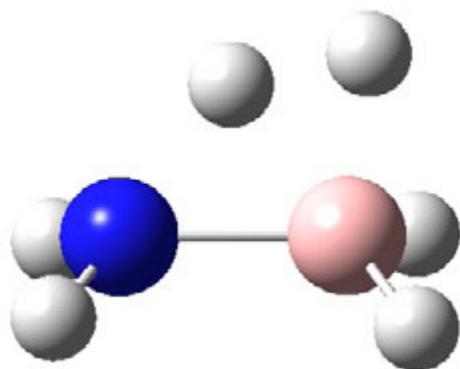
H<sub>3</sub>AINH<sub>3</sub>



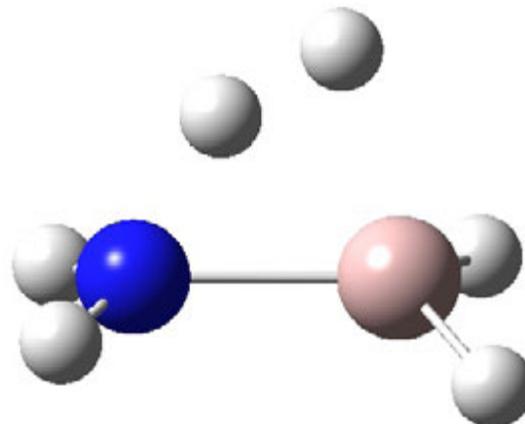
H<sub>3</sub>AIPH<sub>3</sub>

“Thermodynamic Properties of Molecular Borane Phosphines, Alane Amines, and Phosphine Alanes and the [BH<sub>4</sub>][PH<sub>4</sub><sup>+</sup>], [AlH<sub>4</sub>][NH<sub>4</sub><sup>+</sup>], and [AlH<sub>4</sub>][PH<sub>4</sub><sup>+</sup>] Salts for Chemical Hydrogen Storage Systems from Ab Initio Electronic Structure Theory,” D. J. Grant and D. A. Dixon *J. Phys. Chem., A* **2005**, *109*, 10138

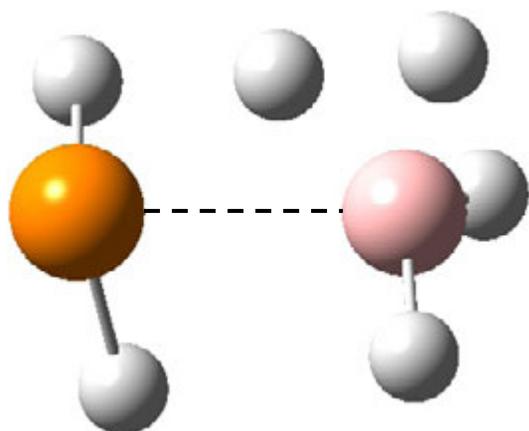
$\text{BH}_2\text{NH}_2\cdots\text{H}_2$  (TS)



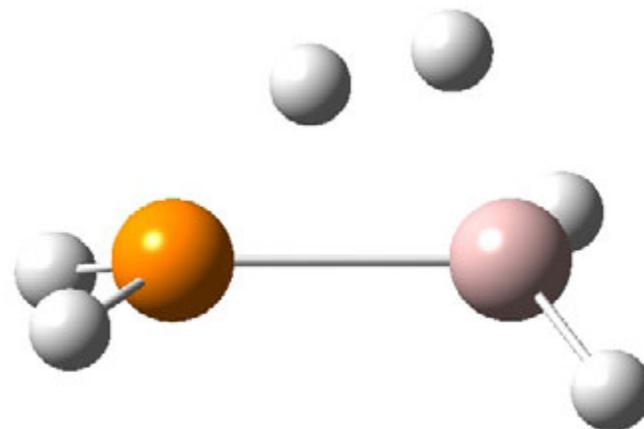
$\text{AlH}_2\text{NH}_2\cdots\text{H}_2$  (TS)



$\text{BH}_2\text{PH}_2\cdots\text{H}_2$  (TS)



$\text{AlH}_2\text{PH}_2\cdots\text{H}_2$  (TS)

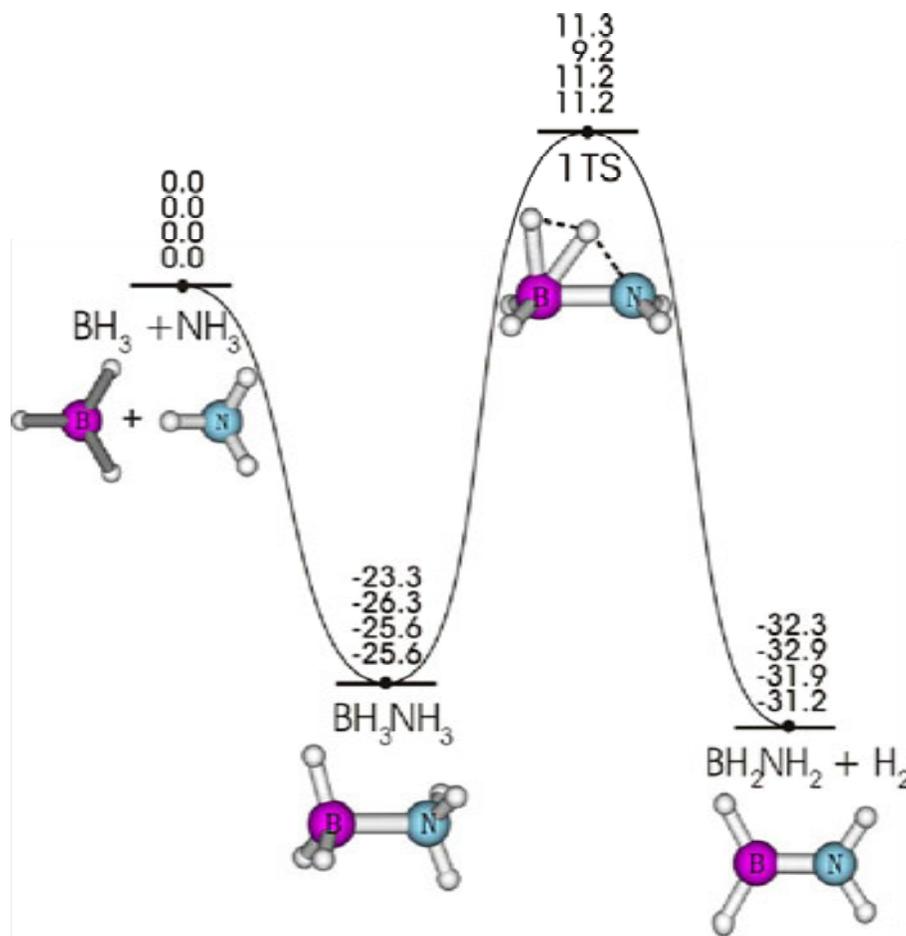


# Energetics (kcal/mol) for the Release of H<sub>2</sub> (gas phase products)

Reaction	$\Delta H$ (298K)	TS Energy	Bond Energy
$\text{AlH}_3\text{NH}_3 \rightarrow \text{AlH}_2\text{NH}_2 + \text{H}_2$	5.0	27.6	26.1
$\text{AlH}_2\text{NH}_2 \rightarrow \text{HAlNH} + \text{H}_2$	61.9		
$\text{AlHNNH} \rightarrow \text{AlN} + \text{H}_2$	74.9		
$\text{BH}_3\text{PH}_3 \rightarrow \text{BH}_2\text{PH}_2 + \text{H}_2$	17.4	30.4	21.1
$\text{BH}_2\text{PH}_2 \rightarrow \text{HBPH} + \text{H}_2$	31.4		
$\text{BHPH} \rightarrow \text{BP} + \text{H}_2$	82.5		
$\text{AlH}_3\text{PH}_3 \rightarrow \text{AlH}_2\text{PH}_2 + \text{H}_2$	5.6	34.4	14.0
$\text{AlH}_2\text{PH}_2 \rightarrow \text{HAIPH} + \text{H}_2$	34.6		
$\text{AlHPH} \rightarrow \text{AlP} + \text{H}_2$	45.4		
$\text{BH}_3\text{NH}_3 \rightarrow \text{BH}_2\text{NH}_2 + \text{H}_2$	-8.3	34.5	25.9
$[\text{BH}_4^-][\text{PH}_4^+] (\text{s}) \rightarrow \text{BH}_3\text{PH}_3 + \text{H}_2$	-13.2		
$[\text{AlH}_4^-][\text{NH}_4^+] (\text{s}) \rightarrow \text{AlH}_3\text{NH}_3 + \text{H}_2$	-3.3		
$[\text{AlH}_4^-][\text{PH}_4^+] (\text{s}) \rightarrow \text{AlH}_3\text{PH}_3 + \text{H}_2$	-9.3		

- Isoelectronic species – no obvious advantage energetically and less capacity due to mass.
- Direct H<sub>2</sub> elimination above dative bond energy – need catalysts.

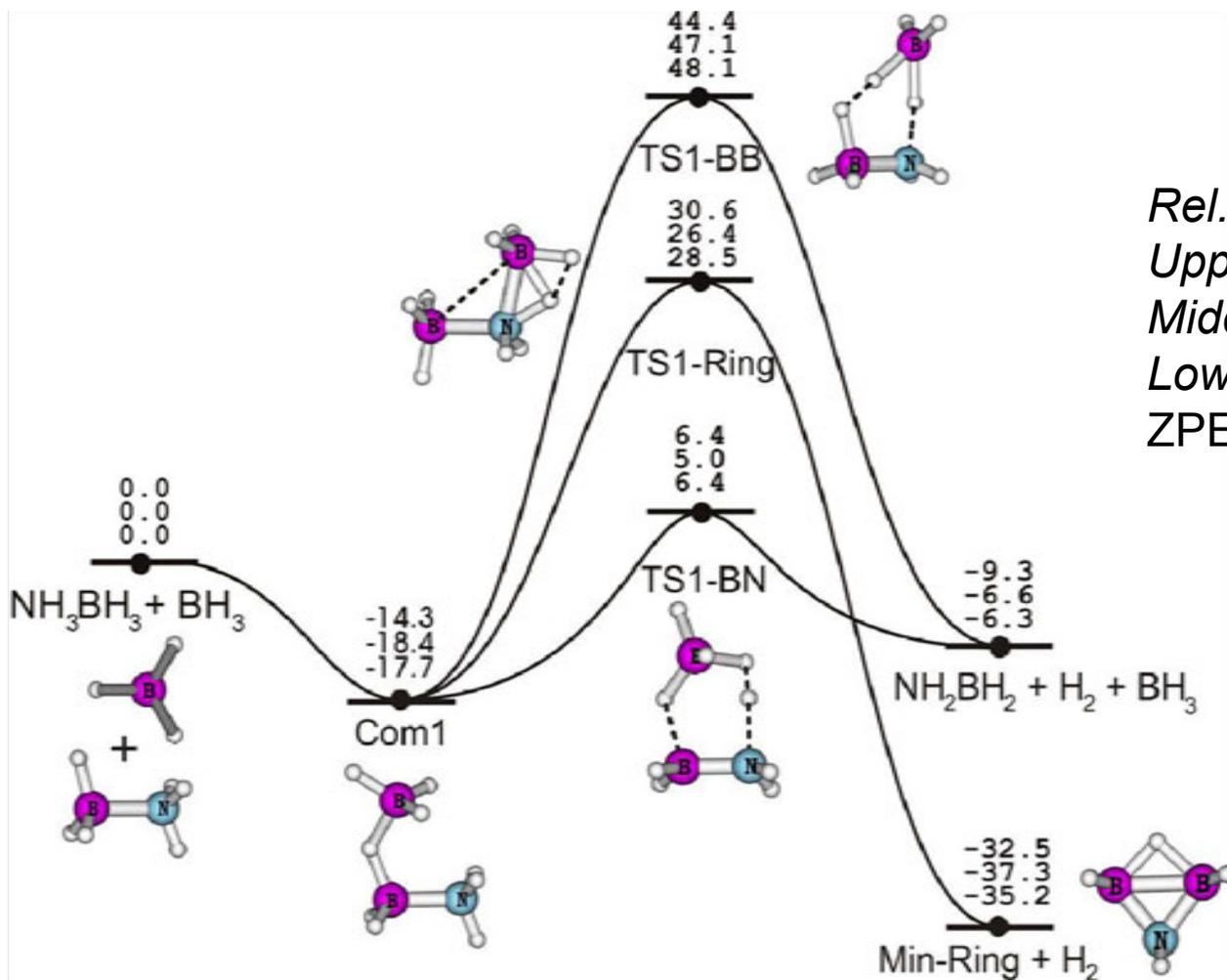
# Reaction Pathway for H<sub>2</sub>-Generation from BH<sub>3</sub>NH<sub>3</sub>



Relative energies in kcal/mol: Upper:  
B3LYP  
Middle: MP2 and CCSD(T)//MP2  
Lower: CCSD(T)//CCSD(T)  
using aug-cc-pVTZ basis set.  
ZPE: MP2/aug-cc-pVTZ

B-N bond cleavage is energetically more favored over the unimolecular H<sub>2</sub> release from borane amine

# Pathways for H<sub>2</sub>-Generation from BH<sub>3</sub>NH<sub>3</sub> + BH<sub>3</sub>

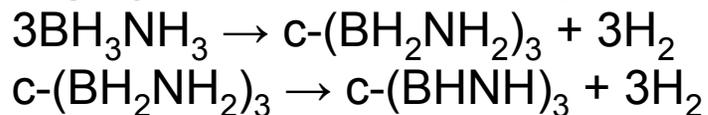


*Rel. energies in kcal/mol:*  
 Upper: B3LYP  
 Middle: MP2  
 Lower: CCSD(T)//MP2  
 ZPE: MP2/aVTZ

BH<sub>3</sub> can serve as a catalyst for H<sub>2</sub> elimination from BH<sub>3</sub>NH<sub>3</sub>.

# Cyclization reaction energetics in the gas phase in kcal/mol

## Highly accurate CCSD(T)/CBS

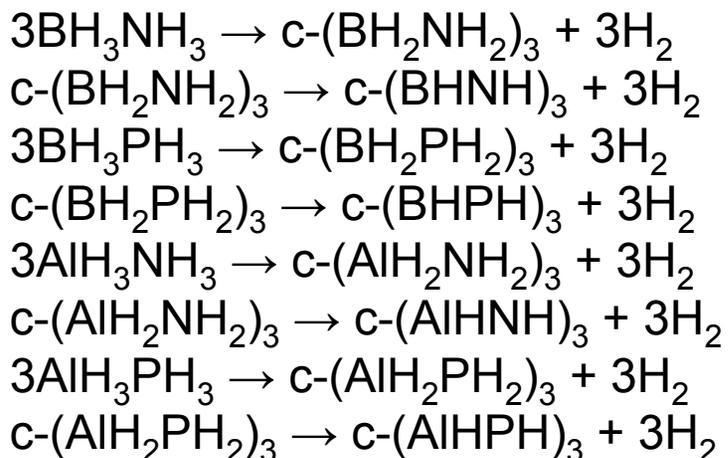


$\Delta\text{H}$  (298K)

-54.5

-20.4

## G3MP2



$\Delta\text{H}$  (298K)

-60.8

-23.4

-49.1

57.0

-83.6

25.1

-64.7

17.2

- Very exothermic processes in the gas phase. Need to investigate condensed phase energetics.
- Key issues are the heat of fusion and vaporization of  $\text{BH}_3\text{NH}_3$  and the associated intermolecular interactions.

# Conclusions

- Electronic structure methods can be used to get highly accurate values of the thermodynamic properties of compounds related to fuels for combustion and hydrogen storage.
- Chemical hydrogen storage offers a significant opportunity for enabling the hydrogen economy as well as for SCRAMJet applications.
- We already have some potential materials – borane amines and carbenes as well as others (substituted NN compounds).
- We are designing affordable chemical materials and reactions that permit:
  - adequate hydrogen storage in terms of weight percent
  - acceptable stability until exposed to catalyst or activator
  - controlled evolution of hydrogen at usable pressure when catalyzed or activated
  - efficient (reasonable cost), safe regeneration